Thermal Conductivity Measurements with the Differential Scanning Calorimeter

Introduction

The Perkin-Elmer differential scanning calorimeter (DSC) monitors the heat flow entering two pan-shaped chambers mounted side by side on top of a pair of resistance thermometers.[1] Heat is introduced through the flat-bottom surface of each chamber, and the recorded output shows the difference in heat flow rates, if any, necessary to maintain the base of both chambers at the same designated temperature. It was thought that this would offer a new means of measuring thermal conductivities of cylindrical specimens placed upright in each chamber.

Apparatus

An appropriate mounting (Fig. 1) was constructed, which included a common, upper metal plate with attached thermocouples for measurement of the heat-sink temperature. The temperature gradient across the samples was established by allowing the upper plate to reach a steady-state condition with respect to ambient temperature and by observing the difference between the heat-sink temperature and the digital setting of the DSC. The mounting assembly was supported by an aluminum radiation shield capped by an ebonite insulating disk. The latter had two holes drilled so as to align the cylindrical samples with the sample holders of the DSC. To reduce contact resistances, an oil of high thermal conductivity was placed on both ends of the cylindrical samples (the oil used is Kontaktöl, which is available from the Dynatech Corporation, Cambridge, Mass.). Better control of the temperature gradient would, of course, be available if the upper plate were thermostated.

Methods of Measurement

With this apparatus two methods of measurement are available. The first depends on the use of two cylinders of identical size and shape (an unknown, x, and a reference, R). With the recorded DSC output and the value of ΔT across the pair it is possible, once steady-state conditions are achieved, to determine the thermal conductivity of the unknown by using the Fourier equation of heat flux. Thus (see Fig. 2),

$$q_1 = k_R(A/L)(T - t) \tag{1}$$

$$q_2 = k_x(A/L)(T - t) \tag{2}$$

$$\text{DSC output} = q_1 - q_2 \tag{3}$$

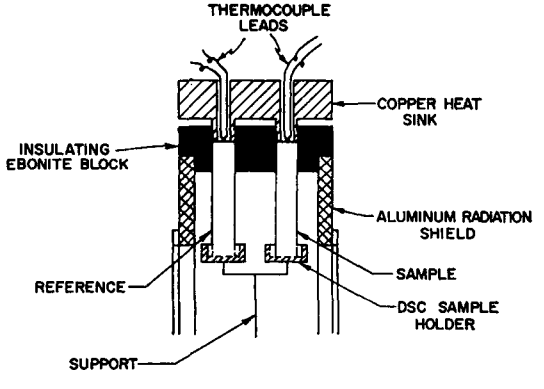

Fig. 1. Thermal conductivity device for the differential scanning calorimeter.

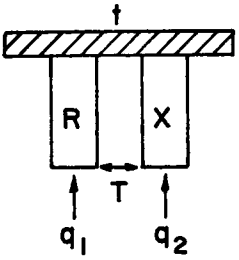

Fig. 2. Schematic representation of heat fluxes and temperatures for DSC thermal conductivity determination.

where the knowns are $q_1 - q_2$ = DSC output, A = cross-sectional area, L = length, T = DSC temperature setting, t = thermocouple readout, and k_R = thermal conductivity of reference.

Subtracting eq. (2) from eq. (1),

$$q_1 - q_2 = (A/L)(T - t)(k_R - k_x) \tag{4}$$

or

$$k_x = k_R - (q_1 - q_2)/(A/L)(T - t) \tag{5}$$

In the second, a somewhat simplified one, only the unknown cylinder is used, while the reference side is capped to suppress its heat loss. During this operation q_1 approximates 0, and the DSC output becomes q_2. Thus, k_x is calculated directly from eq. (2). The zero baseline, or $q_1 = q_2 = 0$, is achieved by operating the DSC at room temperature; that is, the digital setting of the DSC corresponds to ambient temperature.

Results

The second method has been evaluated by test measurements on polytetrafluoroethylene (PTFE) cylinders. In Table I are the results of four runs, which indicate the reproducibility obtainable.

TABLE I
Thermal Conductivity of PTFE

Run no.	Thermal conductivity ($\times 10^{-4}$), cal./(sec.-cm.^{2})(°C.-cm.)	T, °C.	t, °C.
1	5.20	40.0	21.8
2	5.35	40.0	27.4
3	5.72	40.0	27.2
4	5.25	40.0	27.6

The average is 5.38×10^{-4}, the standard deviation is 0.23×10^{-4}, and the literature values[2] are in the range 5.5×10^{-4} to 6.0×10^{-4} cal./(sec.-cm.^{2})(°C./cm.).

A preliminary evaluation of the general two-cylinder technique was made by using PTFE as the reference and polystyrene as the "unknown" material. The thermal conductivity of the "known" PTFE was taken as the average of the four values reported above. The result for polystyrene was 3.0×10^{-4} cal./(sec.-cm.^{2})(°C./cm.); a reported[3] value is 2.7×10^{-4}. A determination of the applicability of this technique to the measurement of the thermal conductivities of composite systems, particularly fiber matrices, is to be carried out.

References

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